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Thermodynamic Considerations on Desulfurization of Cast Iron in Vacuum Melting*

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Synopsis

In order to explain the desulfurization process in vacuum melting of cast iron, the alloy systems of Fe-S, Fe-C-S, Fe-Si-S, and Fe-C-Si-S were melted in vacuum, and considerable desulfurization was recognized in Fe-C-S, Fe-Si-S, and Fe-C-Si-S alloys. The desulfurization process was considered from the equilibrium conditions for desulfurization reactions. Relations between the desulfurization and the concentrations of carbon and silicon in Fe-C-S, Fe-Si-S, and Fe-C-Si-S alloys were explained on the basis of the phase rule. An Fe-C-S alloy was also melted in vacuum in a graphite crucible at 1300~1700°C, and the comparison was made between the experimental results and those calculated from equilibrium relation derived from thermodynamic data.

I. Introdudtion

It has been reported by the present author(1) that cast iron containing sulfur is strongly desulfurized by vacuum melting. Even in low sulfur concentration, the structure of cast iron is strongly influenced by the sulfur concentration. Therefore, the property of cast iron, when melted in vacuum, is considerably affected not only by degassing such as deoxidation but also by desulfurization. Since vacuum melting comes recently to be largely put in practice, the study on the desulfurization of cast iron in vacuum melting is desirable.

Recently, Fischer and Hoffmann(2) have pointed out the formation of the compounds of carbon and sulfur as desulfurization process from experiments on the desulfurization in vacuum melting of Fe-C-S alloy.

In Fe-Si-S and Fe-C-Si-S alloys, accurate thermodynamic data on silicon sulfides have not yet been obtained, and so it is undesirable to depend on thermodynamic consideration alone. Fortunately, the experiments with silicon sulfide were made by Oelsen and Maetz, so, in the present case, considerations about Fe-Si-S and Fe-C-Si-S alloys were made by reference to their experimental results.

II. Experimental procedure

Vacuum melting was carried out by using a high frequency induction furnace and a molybdenum wire wound resistance furnace. In the induction furnace, 100g of metal could be readily melted under vacuo at 1300~1700°C, and all the

* The 988th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in Journal of the Japan Institute of Metals, **23** (1959), 489.

(1) M. Homma and R. Ohno, J. of the Japan Foundrymen's Soc., **29** (1957), 236.

(2) W.A. Fischer u. A. Hoffmann, Arch. Eisenhütt., **29** (1958), 339.

melts were cast into metal mold under vacuo. The molybdenum furnace was a simple resistance furnace which was made gas-tight. The crucibles used were made from the pure graphite rod containing less than 0.1 per cent ash as shown in Fig. 1. Each crucible had two cavities drilled into it so that two samples could be used at the same time. The sample used was of about 10g. By using this apparatus, vacuum melting at temperatures up to about 1400°C could readily be carried out.

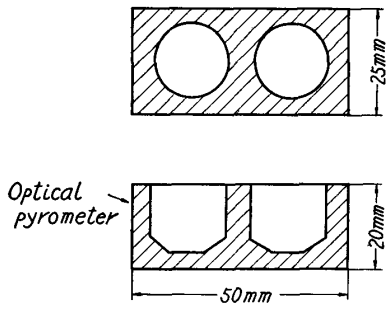

Fig. 1. Diagram of graphite crucible.

The metal samples used were made by adding gas carbon, sulfur, and metallic silicon to electrolytic iron melted under flux covering in air by using a H. F. furnace. Their compositions are shown in Table 1.

The analyses of sulfur, carbon, and silicon were made by combustion volumetric, gravimetric or combustion volumetric, and gravimetric method respectively.

Table 1. Chemical composition of ferro-alloys.

Alloy No.	Composition, %				
	C	Si	S	Mn	P
A-5	3.91	3.06	0.027	0.005	0.006
A-3	3.88	3.18	0.048	0.008	0.002
3112-4	3.52	2.79	0.13	0.007	0.0001
3112-5	2.94	1.90	0.13	0.047	0.0001
3112-1	0.31	6.90	0.16	0.004	0.001
3112-2	0.26	3.01	0.17	0.006	0.001
3205-9	0.048	2.61	1.25	0.001	0.001
3205-10	0.028	2.83	0.65	0.001	0.001
C-4	3.94	0.074	0.026	trace	0.002
3112-3	3.34	0.047	0.13	0.006	0.0002
3203-11	—	—	0.075	—	—
3208-1	—	0.016	0.19	—	—

III. Experimental results and considerations

(1) Fig. 2 shows the results obtained by vacuum-melting Fe-C-S (C-4) and Fe-C-Si-S (A-5, A-3) alloys at 1350°C for 15, 30, and 60 minutes in the molybdenum furnace. The desulfurization rate of Fe-C-Si-S (A-5) alloy was fast compared with that of Fe-C-S (C-4) alloy, and their sulfur concentrations after 15 minutes showed approximately the fixed values of 0.005 and 0.01 per cent respectively. The sulfur concentration of the Fe-C-Si-S (A-3) alloy after 60 minutes was also the same as that of the Fe-C-Si-S (A-5) alloy after 60 minutes.

Fig. 3 shows the results obtained by vacuum melting of Fe-S, Fe-C-S, Fe-Si-S, and Fe-C-Si-S alloys in the H.F. induction furnace. The melting temperature

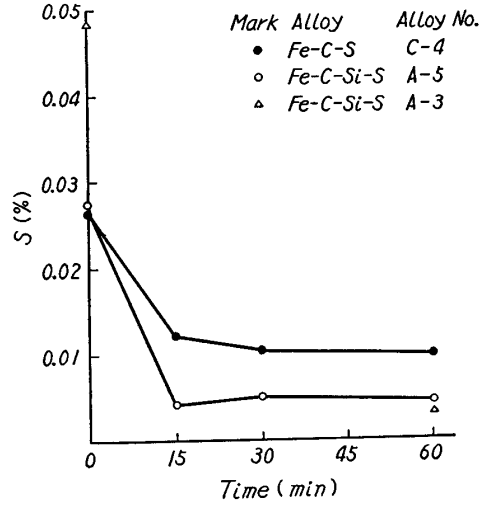

Fig. 2. Relation between sulfur content of Fe-C-S and Fe-C-Si-S alloys and time of vacuum melting in graphite crucible at 1350°C.

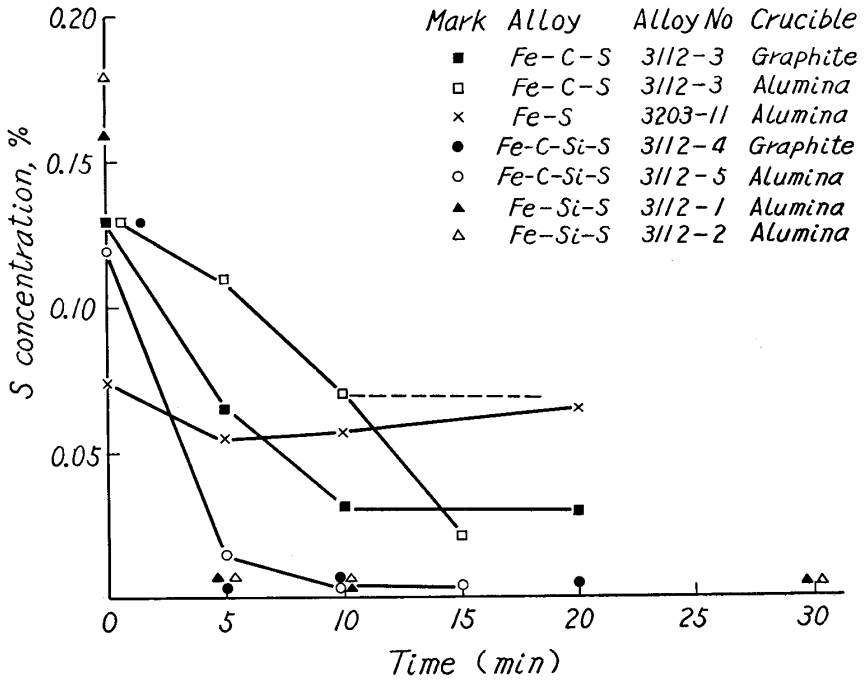

Fig. 3. Desulfurization of various alloys in vacuum melting at 1600°C.

was 1600°C. The crucibles used in this case were prepared from the graphite rod containing less than 0.1 per cent ash and alumina crucibles on the market for vacuum melting. In melting of Fe-Si-S alloys, the alumina crucibles alone were used.

In the case of an Fe-S alloy, desulfurization occurred in 5 minutes, but thereafter sulfur concentration increased with time.

In the case of melting an Fe-C-S alloy in the graphite crucible, desulfurization proceeded for the initial 10 minutes until sulfur concentration showed a fixed value of about 0.03 per cent. When the alumina crucible was used, further

desulfurization proceeded after the initial 10 minutes, sulfur concentration becoming lower than that in the case of graphite crucible.

This progress of desulfurization is considered to be due to silicon entering into the melt from the crucible by the reaction of carbon in the alloy and SiO_2 constituting the crucible, as will be explained later. If this entering did not occur, the sulfur concentration would change in the direction shown by dotted line in Fig. 3.

The desulfurization rates of both Fe-Si-S and Fe-C-Si-S alloys were fast, compared with that of the Fe-C-S alloy, and both of them were strongly desulfurized, 5 to 10 minutes after their sulfur concentrations lowering to a fixed value of 0.005 per cent regardless of their initial sulfur concentrations.

(2) The following chemical reactions can be considered as desulfurization process in the alloy system of Fe-C-Si-S in the vicinity of 1600°C:

$$\underline{S}=1/2S_2(g), \tag{1}$$

$$\underline{S}=S(g), \tag{2}$$

$$\underline{C}+\underline{S}=CS(g), \tag{3}$$

$$\underline{C}+2\underline{S}=CS_2(g), \tag{4}$$

$$\underline{Si}+2\underline{S}=SiS_2(g), \tag{5}$$

and

$$\underline{Si}+\underline{S}=SiS(g), \tag{6}$$

where $\underline{S}$, $\underline{C}$, and Si denote sulfur, carbon, and silicon dissolved in these alloys respectively, and (g) denotes gaseous state. Desulfurization reactions in the most simple system Fe-S are (1) and (2). When carbon or silicon is alloyed to the Fe-S system, the reactions (3) and (4) or (5) and (6) are considered respectively together with the reactions (1) and (2).

Furthermore, in addition to the above reactions, the reactions forming $S_6(g)$ and $S_8(g)$ can be considered in each alloy. However, these reactions may be ignored since equilibrium pressures of S_6 and S_8 are much lower than those of the other components, according to the data compiled by Richardson and Jeffes.[3]

In Fe-S alloy or low carbon steel melted in air, the reactions forming SO(g), $SO_2(g)$, $SO_3(g)$ or COS(g) must also be considered as desulfurization process.

According to the estimation by Chipman[4] from the standard free energy change ΔF° for the formation of $SO_2(g)$, the equilibrium pressure of SO_2 over the iron melt containing 0.05 per cent S and 0.02 per cent O is 2×10^{-8} atm (1.52×10^{-5} mmHg). Since the alloy of high carbon and silicon concentrations such as cast iron contains very little oxygen, desulfurization processes concerning S-O reaction can be ignored.

The following relations (7)~(10) are established between sulfur concentration

(3) F.D. Richardson and J.H.E. Jeffes, J. Iron Steel Inst., **171** (1952), 165.
(4) AIME, *Basic Open Hearth Steelmaking*, (1951), 681.

(weight percentage) in the alloys and equilibrium pressures of S, S_2, CS, and CS_2:

$$\log P_{S_2}=2\log f_S[S\%]-\frac{2\Delta F^\circ_1}{2.303RT}, \tag{7}$$

$$\log P_S=\log f_S[S\%]-\frac{\Delta F^\circ_2}{2.303RT}, \tag{8}$$

$$\log P_{CS}=\log a_C+\log f_S[S\%]-\frac{\Delta F^\circ_3}{2.303RT}, \tag{9}$$

and

$$\log P_{CS_2}=\log a_C+2\log f_S[S\%]-\frac{\Delta F^\circ_4}{2.303RT}. \tag{10}$$

Here the symbols of the type P_{S_2} denote partial pressure of each component in equilibrium. ΔF°_1, ΔF°_2, ΔF°_3, and ΔF°_4 correspond to the standard free energy changes in Eqs. (1), (2), (3), and (4) respectively. The standard states for S, C and gaseous components, i.e., S, S_2, CS, and CS_2 are infinitely dilute solution, graphite, and 1 atm respectively. The values of ΔF° corresponding to each reaction are shown in Table 2 together with references.

Table 2. Thermodynamic data used.

Reaction	Standard Free Energy Equation	Reference
$1/2\ S_2=S$	$\Delta F^\circ=+43{,}250-14.60T$cal	5
$C+S_2=CS_2$	$\Delta F^\circ=-3{,}100-1.73T$cal	3
$C+1/2S_2=CS$	$\Delta F^\circ=+59{,}000-22.75T$cal	6
$S=1/2S_2$	$\Delta F^\circ=+28{,}180-3.44T$cal	7

S denotes infinitely dilute solution of sulfur in pure iron.

By taking f_S to be unity in Eqs. (7) and (8), P_{S_2} and P_S over Fe-S alloy at 1600°C are expressed as follows:

$$P_{S_2}=8.51\times10^{-6}\times[S\%]^2\ \text{atm}, \tag{11}$$

and

$$P_S=4.07\times10^{-5}\times[S\%]\ \text{atm}. \tag{12}$$

In carbon-saturated Fe-C-S alloy, since $f_S=7$ (when $f_S=1$ in Fe-S alloy) at 1600°C according to the results of Finchan and Bergman,[6] and $a_C=1$, P_{S_2}, P_S, P_{CS}, and P_{CS_2} are expressed as follows:

$$P_{S_2}=3.89\times10^{-4}\times[S\%]^2\text{atm}, \tag{13}$$

$$P_S=2.75\times10^{-4}\times[S\%]\text{atm}, \tag{14}$$

$$P_{CS}=2.46\times10^{-4}\times[S\%]\text{atm}, \tag{15}$$

and

$$P_{CS_2}=2.19\times10^{-3}\times[S\%]^2\text{atm}. \tag{16}$$

Of course, the sulfur concentration must be so low that Henry's law is applicable.

(5) G.R. St. Pierre and J. Chipman, JACS, **76** (1954), 4787.
(6) C.J.B. Fincham and R.A. Bergman, J. Metals, **9** (1957), 690.
(7) J.A. Cordier and J. Chipman, Trans. AIME, **203** (1955), 905.

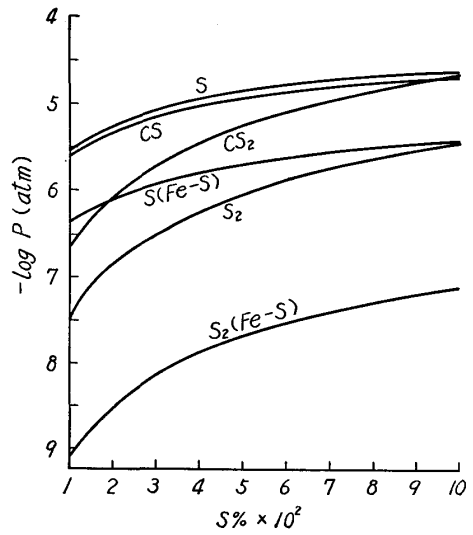

Fig. 4. Equilibrium partial pressures of sulfur species and compounds over Fe-S and carbon saturated Fe-C-S alloys at 1600°C.

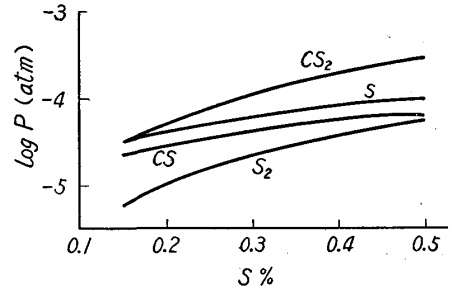

Fig. 5. Partial pressures of CS_2, CS, S_2 and S vs percentage of sulfur (by weight) in carbon-saturated liquid iron at 1600°C according to the results obtained by Fincham and Bergman.

Fig. 4 shows a plot of the equilibrium partial pressure of each component vs. the weight percentage of sulfur in Fe-S and carbon-saturated Fe-C-S alloys according to Eqs. (11)～(16). Fig. 5 shows the equilibrium pressures of CS_2, CS, S_2 and S over carbon-saturated liquid iron-sulfur alloy at 1600°C according to Fincham and Bergman.[6]

If, in vacuum melting, the reactions (1)～(4) are assumed to be approximately in equilibrium state because of large velocity of the reactions, the extent of contribution to desulfurization of each reaction may be qualitatively appreciated from Figs. 4 and 5.

In a certain fixed range of sulfur concentration, the higher the partial pressure of a reaction product is, the larger the extent of contribution to desulfurization of each reaction becomes, and the larger the number of sulfur atom in a molecule of a reaction product is, the larger it becomes. Therefore, in a range of 0.01 to 0.5 per cent S, the contribution of a reaction (4) forming CS_2 is small in low sulfur concentration range, but becomes large with increasing sulfur concentration, compared with those of other reactions. On the contrary, the contribution of the reactions (3) and (2) which form CS and S respectively is large in low sulfur concentration range, but becomes small with increasing sulfur concentration compared with the reaction (4). The reaction (1) forming S_2 has less contribution, as compared with those of other reactions in low sulfur concentration range, but in high concentration range it approaches those of the reactions (3) and (2). Of course, such an appreciation is possible so far as the reactions (1) to (4) are approximately in equilibrium state in the process of vacuum melting as mentioned above. If these reactions are far away from equilibrium, this problem should be explained from the view point of the rate of each reaction.

The initial desulfurization of the Fe-S alloy and the increase in sulfur concentration after 10 minutes in Fig. 3 are considered to be due to S-O reactions and the vaporization of iron which is regarded as a solvent for sulfur. The vapor pressure of iron at 1600°C is 3.89×10^{-2} mmHg.[8] If this desulfurization

(8) O. Kubaschewski, *Metallurgical Thermochemistry*, (1956).

were due to the reactions (1) and (2) forming S_2 and S, the increase in sulfur concentration would not occur. The experimental results show that within the limit of sulfur concentration in Fe-S used, desulfurization by the reactions (1) and (2) will not occur.

Next, the extent of the contribution of each reaction of (1) to (6) for the desulfurization of Fe-Si-S and Fe-C-Si-S alloys mentioned above will be discussed. According to Oelsen and Maetz[9][10][11], when Si is added to the ferro-alloys of high sulfur concentration, SiS (silicon monosulfide) is formed but not SiS_2, and the partial pressure of SiS over the carbon-saturated Fe-C-Si-S alloy containing 5 per cent Si and 0.5 per cent S reaches about 1 atm at 1700°C. Although accurate standard free energy changes for the reactions (5) and (6) have not yet been obtained, the partial pressure of each component in the reactions (1), (2), (5), and (6) in equilibrium with Fe-Si-S alloy at 1600°C was calculated for reference.

By using Eqs. (7) and (8), partial pressures P_{S_2} and P_S in equilibrium with Fe-Si-S alloy containing 3 per cent Si at 1600°C is shown as a function of S percentage as follows:

$$P_{S_2}=2.34\times10^{-5}\times[S\%]^2\text{atm}, \tag{17}$$

and

$$P_S=6.76\times10^{-5}\times[S\%]\text{atm}, \tag{18}$$

which were obtained when $f_S=1.66$ in Eqs. (7) and (8), according to Morris and Williams[12]. Of course, these equations should be applied to dilute solutions below 0.1 per cent S.

Approximate equations of ΔF° for the reactions (5) and (6) at about 1600°C are as follows:

$$\Delta F^\circ_5=-16{,}840+37T\text{cal} \tag{19}$$

and

$$\Delta F^\circ_6=8{,}000-15T\text{cal} \tag{20}$$

respectively. Here the standard states of Si, S, and gaseous components are pure liquid, infinitely dilute solution, and 1 atm respectively. ΔF°_5 was calculated from ΔF°[13] for the reaction $Si(l)+S_2(g)=SiS_2(g)$, and ΔF°_1 for the reaction (1). ΔF°_6 was calculated from ΔF°_1 and ΔF° for the reaction $2Si(l)+S_2(g)=2SiS(g)$. In the calculation of this ΔF°, the following values were used: 84 Kcal[14] for standard change in heat content ΔH° for the reaction $Si(l)=Si(g)$; 86.5 Kcal for ΔH° for the reaction $S_2(g)=2S(g)$, and a dissociation energy of SiS, 147.4± 3Kcal[15], which was derived from spectroscopic measurements. The standard

(9) W. Oelsen u. H. Maetz, Mitt. Kais-Wilh-Inst. Eisenforschung, **21** (1939), 335.
(10) W. Oelsen u. H. Maetz, Arch. Eisenhütt., **13** (1935/40), 469.
(11) W. Oelsen u. H. Maetz, Arch. Eisenhütt., **20** (1949), 53.
(12) J.P. Morris and A.J. Williams Jr, Trans. ASM, **41** (1949), 1425.
(13) AIME, *Basic Open Hearth Steelmaking*, (1951), 573.
(14) J.W. Evans, Trans. AIME, **197** (1953), 655.
(15) S.J.Q. Robinson and R.F. Barrow, Proc. Phys. Soc. (London), **67A** (1954), 95.

entropy change ΔS° for the reaction $2Si(l)+S_2(g)=2SiS(g)$ was assumed to be equal to ΔS°[8] for the reaction $2Si(l)+O_2=2SiO(g)$.

Equilibrium partial pressures of SiS_2 and SiS in Eqs. (5) and (6) may be expressed as a function of ΔF°_5 and ΔF°_6 respectively as follows:

$$\log P_{SiS_2}=\log a_{Si}+2\log f_S[S\%]-\frac{\Delta F^\circ_5}{2.303RT}, \tag{21}$$

and

$$\log P_{SiS}=\log a_{Si}+\log f_S[S\%]-\frac{\Delta F^\circ_6}{2.303RT}. \tag{22}$$

In Eqs. (21) and (22), by equating a_{Si} and f_S to 5.35×10^{-4}[16] and 1.66[12] respectively, the equilibrium partial pressures of SiS_2 and SiS over Fe–Si–S alloy containing 3 per cent Si at 1600°C may be expressed as a function of S percentage as follows:

$$P_{SiS_2}=10^{-9}\times[S\%]^2 \text{ atm}, \tag{23}$$

and

$$P_{SiS}=2\times10^{-1}\times[S\%] \text{ atm}. \tag{24}$$

Of course, Eqs. (23) and (24) should be applied to dilute solutions below 0.1 per cent S. As may be seen from Eqs. (17), (18), (23), and (24), the partial pressure of SiS is very high, as compared with those of SiS_2, S_2, and S, in accordance with the experimental results of Oelsen and Maetz[11].

According to Chipman[17], the effects of C and Si on the activity coefficient of S in the Fe–C–Si–S alloy are expressed by the following equation:

$$f_S=f_S^C\cdot f_S^{Si} \tag{25}$$

where f_S is the activity coefficient of sulfur in Fe–C–Si–S alloy, and f_S^C and f_S^{Si} are represented by the equations $f_S^C=f_S(C)/f'_S$ and $f_S^{Si}=f_S(Si)/f'_S$ respectively in which $f_S(C)$ and $f_S(Si)$ are the activity coefficients of sulfur in Fe–C–S and Fe–Si–S alloys respectively and f'_S is the activity coefficient of sulfur in Fe–S alloy.

Since f_C and f_{Si} also increase by the cooperative effect, as may be seen from Eqs. (7), (8), (21), and (22), P_{SiS_2}, P_{SiS}, P_{S_2}, and P_S over Fe–C–Si–S alloy are higher than those of Fe–Si–S alloy respectively so far as a comparison about fixed sulfur and silicon concentratons is made. Furthermore, in the case of the fixed concentrations of sulfur and carbon, P_{CS_2} and P_{CS} of Fe–C–Si–S alloy are also high, compared with those of Fe–C–S alloy as may be seen from Eqs. (9) and (10). However, the partial pressure of SiS in Fe–C–Si–S alloy is very high, compared with those of the other components as in the case of Fe–Si–S alloy.

Since the partial pressure of SiS which is formed by the reaction (6) is very high as stated above, when the present results of the desulfurization of Fe–Si–S alloy which will be described later, are taken into consideration, it may be said

(16) J. Chipman et al., Acta Met., **2** (1954), 439.
(17) AIME, *Basic Open Hearth Steel Making*, (1951), 680.

that the desulfurization of Fe–Si–S and Fe–C–Si–S alloys is made mainly by the process forming SiS according to the reaction (6), so far as the chemical reaction of (6) is approximately in equilibrium. It is due to the high partial pressure of SiS that the rate of desulfurization of the alloys containing Si is greater than that of the Fe–C–S alloys as shown in Figs. 2 and 3. According to the present experiment, in the case of melting the Fe–C–Si–S alloy 3112–5 with alumina crucibles the rate of desulfurization is slow, compared with that of the Fe–C–Si–S alloy 3112–4, and this is due to the lower concentrations of carbon and silicon in the former, i.e., the lower partial pressure of each gaseous component over the former.

Figs. 6 and 7 show relations between the time of melting and the concentrations of silicon and sulfur in melts in vacuum melting at 1600° and 1700°C of Fe–Si–S alloys containing silicon of 1.49 to 0.22 per cent and sulfur of 0.22 to 0.063 per cent. In this case, the H.F. induction furnace was used. Comparing Fig. 6 with Fig. 7, it may be seen that desulfurization and desiliconization occur at the same time. Therefore, an inference may be made that the desulfurization is made by the reaction of S and Si in (5) or (6). Even in the Fe–Si–S alloy containing only 0.22 per cent Si, considerable desulfurization was observed. When comparisons are made of the Fe–Si–S alloys having the same concentrations of sulfur, it will be seen that the higher the silicon concentration and the temperature are, the larger the rate of desulfurization becomes. In the same system of Fe–Si–S alloy, sulfur concentration in melting at 1700°C is lower than that in melting at 1600°C, but as for the silicon concentration, the reverse is the case.

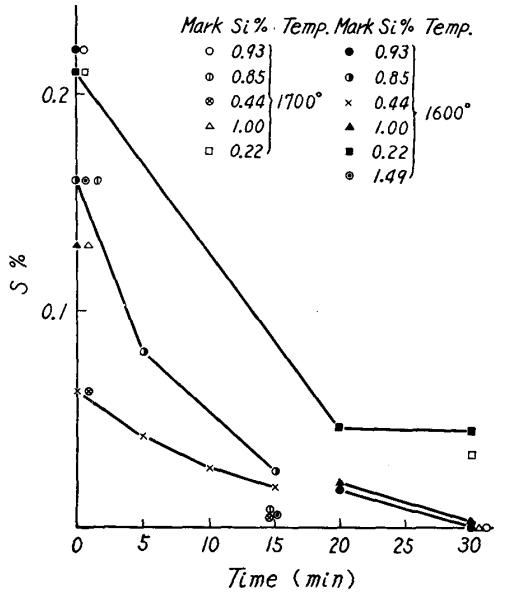

Fig. 6. Desulfurization of Fe–Si–S alloys containing 0.22 to 1.5% Si related to time of vacuum melting at 1600° and 1700°C.

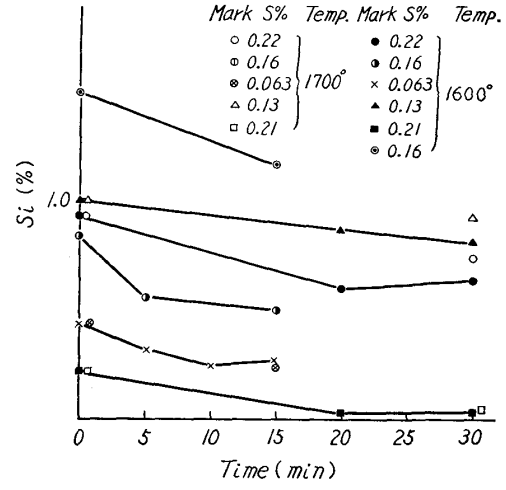

Fig. 7. Decrease of Si contents in the Fe–Si–S alloys containing 0.06 to 0.22% S during vacuum melting at 1600° and 1700°C.

In the Fe–Si–S alloys of high silicon concentration, the conspicuous desulfurization proceeded even 10~15 minutes after contrary to the results shown in Figs. 2 and 3. In melting at 1600°C of an Fe–Si–S alloy of high silicon concentration, the increase in silicon concentration was recognized 20 minutes after which is considered to be due to the vaporization

of iron as will be described later. On the other hand, in the case of an Fe–Si–S alloy of low silicon concentration, an approximately fixed concentration of silicon was maintained during 20 minutes because of small rate of increase in silicon concentration.

The vapor pressure of pure iron at 1600°C is 3.89×10^{-2}mm Hg according to the data compiled by Kubaschewski[8]. The vapor pressure of Si over the Fe–Si alloy can be calculated from the following equation:

$$a_{Si}=\frac{P}{P_O}, \tag{26}$$

where a_{Si} is the activity of Si in Fe–Si alloy, standard state of which is pure liquid silicon, and P_O and P are the vapor pressure of pure liquid silicon and that of silicon in Fe–Si alloy respectively. According to this equation, the vapor pressures of silicon over the Fe–Si alloys containing 3 per cent Si and 1 per cent Si are 4×10^{-4} and 1×10^{-4}mmHg at 1600°C respectively. The values of a_{Si} and P_O are quoted from the results of Chipman *et al.*[16] and the data by Kubaschewski[8] respectively. Comparing these values of vapor pressure of silicon with that of iron, it will be seen that Si concentration can increase during vacuum melting. The higher concentrations of Si in the alloys melted for 30 min at 1700°C are due to the higher vapor pressure of iron leading to the more violet vaporization.

Table 3 shows the changes in S and Si concentrations of Fe–Si–S and Fe–Si

Table 3. Variation of sulfur and silicon contents in Fe–Si and Fe–Si–S alloys by vacuum melting.

Alloy No.	Temp. (°C)	Si %	S %	ΔSi	ΔS	ΔS/ΔSi
3205-9		2.61	1.25			
3205-13	1600	1.44	0.006	− 1.17	− 1.24	1.06
3205-10		2.83	0.65			
3205-14	1600	2.13	0.006	− 0.70	− 0.64	0.91
3205-11		2.72	0.014			
3205-15	1600	2.91	0.003	+ 0.19	—	—
3208-4		0.22	0.21			
3208 26	1600	0.032	0.045	− 0.188	− 0.165	0.88
3208-29	1700	0.037	0.034	− 0.183	− 0.176	0.96

alloys in vacuum melting for 30 minutes at 1600°C and 1700°C. The alloys 3208–26 and –29 were obtained by vacuum melting of the alloy 3208–4. The alloys 3205–13 and –14 were obtained from the alloys 3205–9 and –10 respectively, and the alloy 3205–15 from the Fe–Si alloy 3205–11. In the case of Fe–Si–S alloys, the ratios of desulfurized to desiliconized amount, ΔS/ΔSi, are shown. As shown in Table 3, the Fe–Si–S alloys containing almost the same amount of S, and Si were selected so that the analytical errors of these elements would not affect the value of ΔS/ΔSi. Since the weight ratios S/Si necessary for the the reactions (5) and (6) are 2.28 and 1.14 respectively, all the ratios shown in Table 3 are near 1.14, corresponding to the reaction (6) for the SiS formation.

The ratios of $\Delta S/\Delta Si$ should be larger than 1.14 by the contribution of the other reactions (1), (2), and (5), whereas experimental values were all less than 1.14, as shown in Table 3. As shown in the results of an Fe–Si alloy in Table 3, the effect of the vaporization of iron, i.e., the increase in Si concentration appears, but not the effect of the vaporization of Si, i.e., the decrease in Si concentration. Therefore, the decrease in Si concentration in Fe–Si–S alloy is due to the reaction of S and Si, and the most part of desulfurization in Fe–Si–S alloy may be made by the reaction (6) forming SiS.

The most desulfurization 10 minutes after in vacuum melting of Fe–C–S alloy containing 3.34 per cent C in alumina crucible is due not to the reactions (1) to (4) but to the reaction (6) which forms SiS by the combination of S in the melt and Si entered into the melt according to the reaction

$$SiO_2+2\underline{C}=\underline{Si}+2CO, \tag{27}$$

where SiO_2 is a constituent of the alumina crucible, and $\underline{C}$ is dissolved carbon in the alloy. In fact, Si concentration of the alloy in melting for 15 minutes was 0.24 per cent. As mentioned above, if there were no such entering of Si from crucible, the S concentration would change in the direction shown by dotted line in Fig. 3.

(3) Next, consideration is made of the minimum sulfur concentration attainable by vacuum melting. The equilibrium total pressures of components containing sulfur over the Fe–S, Fe–C–S, Fe–Si–S, and Fe–C–Si–S alloys are expressed by the following equations:

$$P_T(\text{Fe–S})=P_S+P_{S_2}, \tag{28}$$

$$P_T(\text{Fe–C–S})=P_S+P_{S_2}+P_{CS}+P_{CS_2}, \tag{29}$$

$$P_T(\text{Fe–Si–S})=P_S+P_{S_2}+P_{SiS}+P_{SiS_2}, \tag{30}$$

and

$$P_T(\text{Fe–C–Si–S})=P_S+P_{S_2}+P_{CS}+P_{CS_2}+P_{SiS}+P_{SiS_2}. \tag{31}$$

Since a_{Si}, a_C, and f_S increase with increasing Si and C concentrations, the values of P_T also increase with these concentrations as may be seen from Eqs. (7), (8), (9), (10), (21), and (22).

Fig. 8 shows the equilibrium total pressures of sulfur species and sulfur compounds over Fe–S, carbon-saturated Fe–C–S, 3% C Fe–C–S, 3% Si Fe–Si–S, and carbon-saturated 3% Si Fe–C–Si–S alloys vs. S percentage of 0.1 to 0.01. The curve of Fe–S alloy was obtained according to Eqs. (7) and (8). The curves of 3% C Fe–C–S and carbon-saturated Fe–C–S alloys were obtained according to Eqs. (7), (8), (9), and (10). The value of

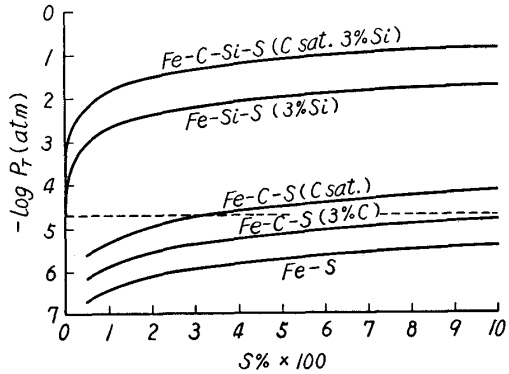

Fig. 8. Equilibrium total pressures (P_T) of sulfur species and sulfur compounds over liquid Fe–S, Fe–C–S, Fe–Si–S, and Fe–C–Si–S alloys at 1600°C, plotted as $-\log P_T$ vs. weight percentage sulfur in the iron.

the activity of carbon (activity of graphite =1) in 3% C Fe–C–S alloy was quoted from the recent results of Turkdogan[18], and those of f_S from the results of Morris and Buehl[19]. The curves referring to 3% Si Fe–Si–S and carbon-saturated 3% Si Fe–C–Si–S alloys were obtained according to Eq. (22) on an assumption that P_T in each alloy is approximately equal to P_{SiS}. a_{Si} and f_S were obtained according to Chipman[16],[17]. The higher the concentrations of C and Si are, the higher the position of the curve is.

The condition determining the sulfur concentration of the alloys in vacuum melting can be considered according to the phase rule

$$F=n+2-P, \tag{32}$$

where F, n, and P are the degrees of freedom, the number of components, and the number of coexisting phases respectively. Considering a most complicated system, i.e., Fe–C–Si–S alloy, so far as the substance constituting a crucible does not react with the alloy, $n=4$ and $P=2$; hence, $F=4$. Therefore, if the temperature of the system, P_T, and the concentrations of carbon and silicon are fixed, sulfur concentration is determined. When a graphite crucible is used, $F=3$; hence, if the concentration of silicon besides temperature and P_T is fixed, sulfur concentration is determined. Similarly, in the other systems, if temperature and the others besides P_T are fixed, sulfur concentration is determined.

Now, if the total pressures P_T of components containing sulfur over the alloys are fixed in accordance with vacuum melting condition, S concentration in a melt is determined in so far as the other conditions mentioned above are fixed. Drawing adequately a dotted line corresponding to the total pressure P_T which was assumed to be determined by vacuum melting condition in Fig. 3 in order to explain the order of the magnitudes of sulfur concentrations in each alloy melted in vacuum, S percentage corresponding to the intersections of the dotted line and each curve are of the alloy in equilibrium with P_T, i.e., the minimum sulfur concentrations obtainable in vacuum melting. In Fe–S, 3% Fe–C–S, C–saturated Fe–C–S, 3% Si Fe–Si–S, and C–saturated 3% Si Fe–C–Si–S alloy, attainable S percentage should decrease in the order named, although its difference in 3% Si Fe–Si–S and C–saturated 3% Si Fe–C–Si–S alloy is very small. The results of this consideration seem to be in accordance with the experimental results.

It should be noted here that even after a fixed sulfur concentration shown in Figs. 2 and 3, the desulfurization of alloy as well as the vaporization of iron continue so far as evacuation is maintained. In carbon-saturated Fe–C–S alloy, since carbon concentration is fixed even if iron vaporizes, sulfur concentration shows also a fixed value as may be seen from the phase rule as far as vacuum pressure does not change. However, in 3.34% C Fe–C–S alloy in Fig. 3, since C concentration increases with the vaporization of iron, S concentration should be slowly decreased, even if the entering of silicon from the crucible does not

(18) E.T. Turkdogan, L.E. Leak and C.R Masson, Acta Met., 4 (1956), 396.
(19) J.P. Morris and R.C. Buehl, Trans. AIME, 188 (1950), 317.

occur. Although a fixed Si concentration was assumed in the above consideration, it decreases with the proceeding of desulfurization, and on the contrary, it should be gradually increased by the vaporization of iron after the desulfurization. Therefore, sulfur concentration should be gradually decreased even after the first rapid desulfurization.

As shown in Figs. 6 and 7, the concentration of Si and S in the Fe–Si–S alloy, initial Si and S concentrations of which are 0.22 and 0.21 per cent respectively, become 0.32 and 0.045 per cent respectively after vacuum melting for 20 minutes at 1600°C. Since the partial pressure of SiS over the Fe–Si–S alloy containing 0.03 per cent Si is expressed by the equation $P_{SiS}=1\times10^{-3}\times[S\%]$ atm and is approximately the same magnitude as the total pressure of carbon-saturated Fe–C–S alloy, obtainable sulfur concentrations in both alloys should be approximately of the same magnitude, so far as vacuum melting condition is the same in both cases. As a matter of fact, the minimum sulfur concentration obtained in carbon-saturated Fe–C–S alloy was 0.03 per cent, being of the same magnitude as that of the Fe–Si–S alloy.

(4) Next, the relation between minimum sulfur concentration obtainable in vacuum melting and temperature will be discussed. Fig. 9 shows the relation between temperature and S percentage of Fe–C–S (3208–1) melted in vacuum in graphite crucibles at temperatures 1300°C~1700°C. The H.F. induction furnace was used. The time of melting at each temperature was 30 minutes. The calculated values shown in Fig. 9 were obtained by the following procedure: First, the equations of the type $P_T=a[S\%]^2+b[S\%]$ which is related with $P_T(=P_{CS_2}+P_{CS}+P_{S_2}+P_S)$ over carbon-saturated Fe–C–S alloy at 1300°, 1400°, 1500°, 1600°, and 1700°C were derived from Eqs. (7)~(10), a and b being functions of temperature. Then, P_T depending on vacuum melting condition was determined by substituting a value of S percentage obtained in the experiment at 1600°C for S percentage in the equation at 1600°C. Finally, assuming that this value of P_T was independent of temperature, S percentage at other temperatures were calculated by putting this value in the equations at 1300°, 1400°, 1500°, and 1700°C.

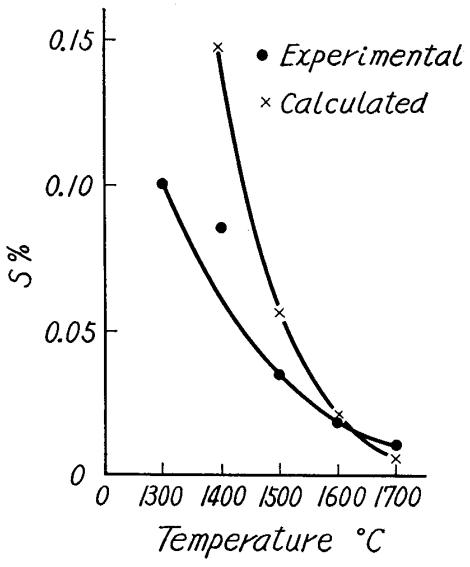

Fig. 9. Sulfur contents (by weight percentage) of carbon saturated Fe–C–S alloy at various vacuum melting temperatures.

The solubility of carbon in iron at each temperature was quoted from the results by Chipman *et al.*[20] Assuming the independence of temperature, the effect of carbon concentration on the activity coefficient of sulfur f_S was calculated according to Morris

(20) J. Chipman et al., Trans. ASM, **44** (1952), 1215.

and Buehl[19].

As shown in Fig. 9, the minimum sulfur concentration obtained in vacuum melting decreases with rising temperature. Although the calculated results also show similar tendency, at temperatures below 1600°C the calculated values are higher than the experimental values, whereas at temperatures above 1600°C the reverse is the case.

This fact shows that P_T which is determined by vacuum melting condition depends also on temperature, i.e., values of P_T at temperatures below 1600°C are less than that at 1600°C and those at temperatures above 1600°C are larger than that at 1600°C. This temperature dependence of P_T may be due to the change in the vapor pressure of iron by temperature.

(5) Thus, the bulk of the desulfurization of cast iron in vacuum melting is considered to be made by the reaction which forms SiS. According to Marincek[21], the desulfurization of cast iron in vacuum melting is due to the formation of volatile silicon sulfides; for example, the sublimation point of SiS_2 is about 1200°C. However, since all sulfur species and compounds are in gaseous state at the melting temperature of cast iron, the same may also be said of the sulfur species and compounds except silicon sulfides. According to the present study, this strong desulfurization of cast iron may be explained as follows: It is made not by the formation of SiS_2 but by that of SiS, the free enargy of formation of which is a larger negative value than those of other sulfur compounds and species, i.e., higher equilibrium partial pressure than those of the latter.

In an investigation of the manufacture of steel for transformer, Garunuk and Samarin[22] recognized that further desulfurization of steel melt was made by the addition of Fe-Si in vacuum, and for this desulfurization, made an explanation that it occurred by the removal of sulfur from the melt as compounds of S and O or sulfur vapor. However, from the present study, this desulfurization after Fe-Si addition seems to occur by the formation of SiS.

Summary

(1) An Fe-S (0.075%S) alloy is slightly desulfurized at first, and then sulfur concentration increases with time. In vacuum melting at 1600°C and 1350°C of Fe-C-S alloys in graphite crucibles, desulfurization proceeds until fixed values of sulfur concentration are attained 10 or 15 minutes after. In vacuum melting of an Fe-C-S alloy in alumina crucibles, the desulfurization velocity is first slow as compared with that of the melting in graphite crucibles but it becomes fast with time, sulfur concentration becoming lower than that of the melting in graphite crucibles after 15 minutes.

(2) It is considered that the desulfurization of the Fe-S alloy is due to S-O reactions $\underline{S}+\underline{O}=SO(g)$, $\underline{S}+2\underline{O}=SO_2(g)$, and $\underline{S}+3\underline{O}=SO_3(g)$, and that the increase in sulfur concentration is due to the vaporization of iron. As desulfurization

(21) B. Marincek, Rev. Met., **53** (1956), 67.
(22) G.A. Garunuk and A.M. Samarin, Izvest. Akad. Nauk, SSSR, OTN No. 5 (1957), 77.

reactions of the Fe-C-S alloys, reactions $\underline{S}=1/2S_2(g)$, $\underline{S}=S(g)$, $\underline{C}+S=CS(g)$, and $\underline{C}+2\underline{S}=CS_2(g)$ are considered. If in the process of vacuum melting each reaction is approximately in equilibrium, as far as desulfurization in the range 0.01 to 0.5 per cent S is concerned, the Fe-C-S alloys are mainly desulfurized by the reactions $\underline{C}+\underline{S}=CS(g)$, $\underline{C}+2\underline{S}=CS_2(g)$, and $S=S(g)$ in the range of low sulfur concentration and by the reaction $\underline{C}+2\underline{S}=CS_2(g)$ in the range of high sulfur concentration. The further lowering of sulfur concentration in melting of the Fe-C-S alloy in alumina crucibles is due to the entering of Si into the alloy, and if this did not occur, sulfur concentrations 15 minutes after would be higher than those of the melting in graphite crucibles. Considering from thermodynamic equilibrium condition, the obtainable minimum sulfur concentration in vacuum melting of Fe-C-S alloy should decrease with increasing carbon concentration.

(3) In vacuum melting of an Fe-C-S alloy in graphite crucibles, obtainable minimum sulfur concentration decreases with increasing temperature. This tendency is in accordance with the results derived thermodynamically from equilibrium condition.

(4) The rates of the desulfurization of Fe-Si-S alloys containing high silicon as well as Fe-C-Si-S alloys are fast compared with those of Fe-C-S alloys, and the obtainable minimum sulfur concentrations in the former are low compared with those in the latter. In the case of vacuum melting of Fe-Si-S alloys at 1600° and 1700°C, desiliconization occurs simultaneously with desulfurization; the higher the silicon concentration of the alloy is, the lower the sulfur concentration of it becomes; the sulfur concentration obtained in melting at 1700°C is low compared with that obtained in melting at 1600°C so far as a comparison is made on the same alloys; even in the case of 0.22 per cent Si considerable desulfurization occurs. In the case of vacuum melting of Fe-Si-S alloys containing approximately the same amount of Si and S, the weight ratios of the decrease in sulfur amount to that in silicon amount closely approximate the weight ratio of the two elements which is necessary to form the silicon monosulfide SiS.

(5) It may be said that the desulfurization of Fe-Si-S and Fe-C-Si-S alloys are made by the reaction which forms SiS provided that the chemical reaction $\underline{Si}+\underline{S}=SiS(g)$ is approximately in equilibrium during vacuum melting, and that the strong desul-furization of these alloys is due to the relatively high equilibrium partial pressure of SiS.

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